100-NR-2 Apatite Treatability Test Plan Implementation

Concurrence to proceed with the Treatability Test Plan addendum for jet injections of a phosphate solution, pre-formed apatite, and combination of both at 100-NR-2 Groundwater Operable Unit.

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1.0 INTRODUCTION

This addendum to the *Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit* (DOE/RL-2005-96) describes the plan for conducting a preliminary field-scale demonstration in the vicinity of the apatite treatability test site. The demonstration will be conducted to evaluate potential strategies for jet injections of three different media: a phosphate solution, pre-formed apatite, and the same phosphate solution followed by the addition of the pre-formed apatite. The demonstration shall determine the implementability of using jet injection technology to inject these media within the vadose zone and upper unconfined aquifer near the shoreline of the Columbia River in the 100-N Area of the Hanford Site. If and where applicable, the "Underground Injection Control" (UIC) regulations, WAC 173-218, will be followed as required for a Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) remedial activity. It should be noted that the *Interim Remedial Action Record of Decision for the 100-NR-1 and 100-NR-2 Operable Units of the Hanford 100-N Area* (IROD) (EPA/ROD/R10-99/112, 1999) specifically granted a waiver to the WAC 218-218, "UIC," regulations for the 100-NR-2 Operable Unit (OU) interim activities under the Statutory Determinations listed on page vi of the IROD.

The remedy specified in the 100-NR-1/2 IROD included operation of a pump-and-treat system as well as a requirement to evaluate alternative strontium-90 treatment technologies. It was recognized from the onset that pump-and-treat was unlikely to be an effective long-term treatment method because of the geochemical characteristics of strontium-90, the primary contaminant of concern. Subsequent performance monitoring has substantiated this expectation. Accordingly, the first CERCLA 5-year review reemphasized the need to aggressively pursue alternative methods to reduce impacts on the Columbia River.

A significant amount of the strontium-90 mass (40% to 70%), in sediments along the Columbia River shoreline at 100-NR-2, is being held in the variably saturated sediments within the zone of water table fluctuation, which is driven by seasonal and diurnal variability in the Columbia River stage (PNNL-16891, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO4 Solution Injection and Sr-90 Immobilization in 100-N Sediments* and PNNL-18303, *Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of a Ca-Citrate-Phosphate Solution*). It is also likely that there is a higher concentration of strontium-90 in low-conductivity zones in this variably saturated zone, due to less water flushing.

With the presentation of the *Evaluation of ^{90}Sr Treatment Technologies for the 100-NR-2 Groundwater Operable Unit* (Letter Report; Fluor/CH2M HILL, 2004) at the December 8, 2004, public meeting, U.S. Department of Energy (DOE), Fluor, Pacific Northwest National Laboratory (PNNL), and the Washington Department of Ecology (Ecology) agreed that a likely response scenario for groundwater remediation at 100-N is apatite sequestration as the primary treatment. This would be followed by a secondary treatment, or polishing step, if necessary (most likely phytoremediation). Since then, the agencies have worked together to identify which apatite sequestration technology has the greatest chance of reducing strontium-90 flux to the river, for a reasonable cost. A low concentration calcium-citrate-phosphate solution for apatite formation was injected into the aquifer through 10 injection wells during FY06 and FY07; the resulting report, *100-NR-2 Apatite Treatability Test: Low-Concentration Calcium-Citrate-Phosphate Injection for In Situ Strontium-90 Immobilization* (PNNL-17429), lead to the development of an additional treatability test plan for high concentration injections in *Meeting Minutes, Unit Manager's Meeting, 100 & 300 Area Groundwater, Source Operable Units, Facility (D4 and ISS), and Mission Completion, May 8, 2008* (0078408).

This field-scale demonstration will be conducted at the upstream end of the Apatite Permeable Reactive Barrier (PRB) and downstream of the Total Petroleum Hydrocarbon (TPH) well (199-N-173). Due to the limited technical risk associated with this activity, a stand-alone treatability test plan will not be prepared. Instead, this activity will be conducted under this addendum to DOE/RL-2005-96, with treatability test specifics documented in a field test instruction to be provided upon contract award.

1.1 BACKGROUND

The Hanford Site is a DOE site located in southeastern Washington State near Richland, Washington (Figure 1-1). The 100 Areas are located along the Columbia River and include nine DOE nuclear reactors previously used for plutonium production. The 100-N Area contains the 100-N Reactor, and is the area where this study will take place.

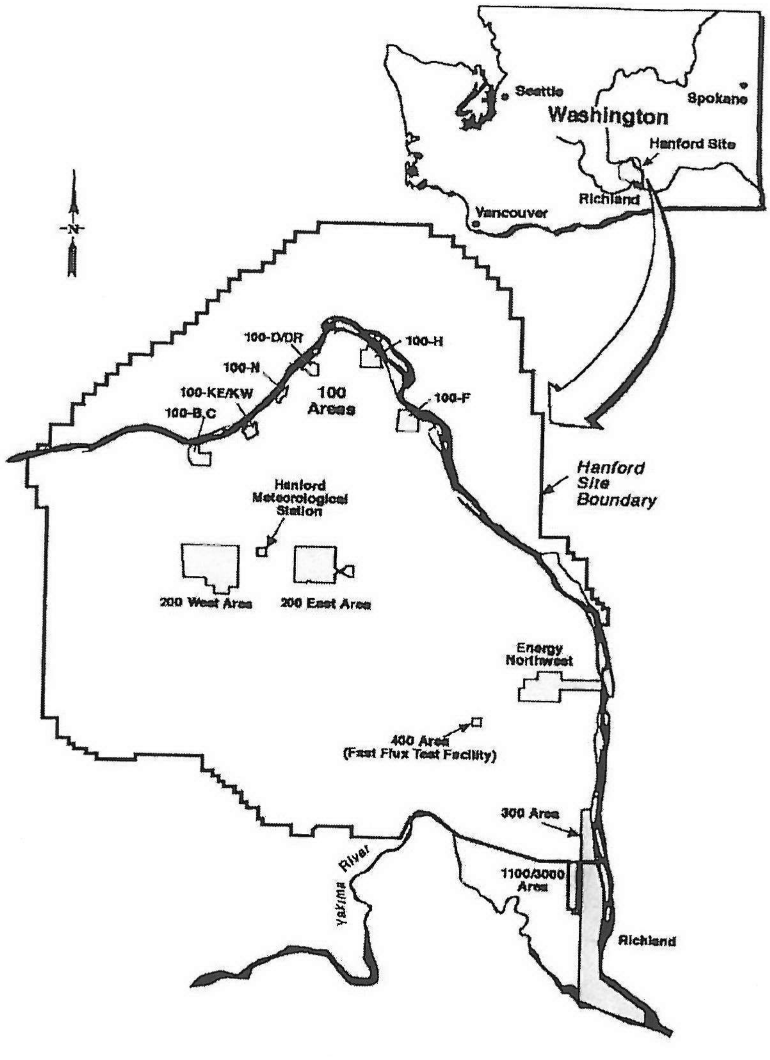

Figure 1-1. Hanford Site and Washington State.

The operation of the 100-N Area nuclear reactor required the disposal of bleed and feed cooling water from the reactor's primary cooling loop, the spent fuel storage basins, and other reactor-related sources. Two crib and trench liquid waste disposal facilities (LWDFs) were constructed to receive these waste streams, and disposal consisted of percolation into the soil. The first LWDF (1301-N) was constructed in 1963, about 800 ft from the river. Liquid discharges to this facility contained radioactive fission and activation products, including cobalt-60, cesium-137, strontium-90, and tritium. Minor amounts of hazardous wastes such as sodium dichromate, phosphoric acid, lead, and cadmium were also part of the waste stream. When strontium-90 was detected at the shoreline, disposal at the first LWDF was terminated. A second crib and trench (1325-N LWDF) was constructed farther inland in 1983 and both continued receiving waste until 1985 when 1301-N was taken out of service. Wastewater discharges to 1325-N ceased in 1991.

A more complete history of the groundwater contamination at 100-N can be found in the *Hanford 100-N Area Remediation Options Evaulation Summary Report* (TAG, 2001). As a result of wastewater disposal practices, soils beneath the LWDFs were contaminated from the surface sediments to the lower boundary of the unconfined aquifer. A portion of the contaminants migrated to the Columbia River via groundwater. To address the contamination, the IROD divided the 100-N Area into two operable units (OU). The 100-NR-1 OU contains all the source waste sites located within the main industrial area around the 100-N Reactor and the Hanford Generating Plant, and includes the surface sediments and shallow subsurface soil associated with the LWDFs. Remedial activities that address the contamination in this unit are ongoing. The 100-NR-2 OU contains the contaminated groundwater, groundwater-surface water interface, discharges/upwellings occurring directly in river, and any sediment below the historical high-water mark (including shoreline).

1.2 SITE DESCRITPION

A thorough discussion on the site specific characteristics such as, but not limited to: geology, hydrogeology, groundwater-river interaction, and nature and extent of strontium-90 contamination can be found in the governing document, DOE/RL-2005-96. The evaluation of strontium-90 treatment technologies, remediation history and justification for previous calcium-citrate-phosphate injections can also be found in that document. The results from the first phase of injections conducted in 2006 and 2007 are documented in PNNL-17429. Increases in strontium-90 and other metals concentrations at monitoring wells and aquifer tubes following the low-concentration injections resulted from the introduction of the higher ionic strength calcium-citrate-phosphate solution and increased calcium concentrations from these injections (discussed further in Section 2.2.2). Similar increases following the high-concentration injections carried out in 2008 were also observed, but to a lesser extent as compared to the low-concentration injections.

2.0 JET INJECTION DEMONSTRATIONS

The primary test objective for the jet injection demonstration is twofold. First, is to evaluate the technology's ability to deliver materials/chemical solutions into the vadose zone and upper unconfined aquifer within three distinct treatment zones in the 100-N Area of the Hanford Site. The use of river water for injection of phosphate and/or pre-formed apatite may be required. Secondly, is to construct a permeable reactive barrier (PRB) to determine the effectiveness for sequestering strontium-90 with a specific amount (~4.0 mg/g) of apatite in the sediment, which allows for the barrier to remain permeable and reactive (PNNL-18303). The approximate location of the three injection treatment zones are depicted in Figure 2-1 and further illustrated in Figure 3-1. The exact injection location(s), amount of chemicals, and method of injection will be determined by Contractor and presented to CHPRC, DOE, and Ecology for review and approval in an Injection Plan following contract award and prior to mobilization.

Previous laboratory experiments in water-saturated sediments (PNNL-16891), field injections (PNNL-17429), and unsaturated sediments (PNNL-18303) have shown that strontium-90 is initially adsorbed to the apatite, then is incorporated into its structure. Because strontium ions (Sr^{2+}) and strontium-90 behave essentially the same as calcium ions (Ca^{2+}), some strontium is incorporated in apatite during the initial precipitation. Thermodynamically, strontiapatite [$Sr_{10}(PO_4)_6(OH)_2$, $K_{sp} = 10^{-51}$] is favored relative to hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, $K_{sp} = 10^{-44}$] (PNNL-16891).

Once solid phase apatite is precipitated, strontium-90 will additionally be incorporated into the apatite structure by solid phase dissolution/recrystallization. The initial step in the process is strontium-90 sorption to the apatite surface. Results of laboratory studies show that this sorption is quite strong [$K_d = 1370 \pm 439$ L/kg] or 55 times stronger affinity than to sediment [$K_d = 24.8 \pm 0.4$ L/kg] (PNNL-18303). The rate of metal incorporation into the apatite crystal lattice can be relatively slow, on the order of days to years. However, in the presence of soluble phosphates, apatite acts as a seed crystal for the precipitation of metal phosphates (Vukovic et al., 1998). Homogeneous nucleation (precipitation directly from solution) will generally not occur except at very high metal concentrations, for example, greater than 10 parts per million (ppm). At low concentrations of the substituting cation (strontium-90 and Ca^{2+}) and in the presence of small amounts of phosphate and a seed crystal of apatite, heterogeneous nucleation occurs on the surface of the apatite seed crystal (Lower et al., 1998). The apatite itself serves as a small, but sufficient source of phosphate to solution, and thus perpetuates the precipitation reaction. Over time, the precipitated metals are sequestered into the apatite crystal matrix. The mechanism (solid state ion exchange) of strontium substitution for calcium in the apatite structure have been previously studied at elevated temperature, but low temperature aqueous rates under Hanford groundwater conditions have only recently been studied (Szecsody et al., 2008 and PNNL-18303).

Descriptions of the three treatment zones are further detailed in the following subsections.

2.1 TREATMENT ZONE AREA CONSIDERATIONS

There were several factors considered during the planning of this treatability test that have provided information on location, schedule, and method of delivery. The locations of the demonstration zones (Figure 3-1) were chosen to maximize the potential for successful application of the jet injection technology, while minimizing interference with ongoing work in the 100-N Area. The positioning of the treatment zones was selected to prevent any effects by the TPH plume, located on the upper plateau inland and up-gradient of the demonstration zones. Figure 3-1 shows the approximate locations of the demonstration zones in relation to Waste Information Data System (WIDS) site 100-N-65, which is associated with a 302,832 liter (80,000 gallon) diesel spill that occurred in 1966. The pink elongated oval illustrated in the figure is the estimated location of a trench that was excavated along the Columbia River bank to intercept the diesel oil before it could reach the river and was periodically burned off during 1967. In 1994, the trench was backfilled with clean material. Data from existing wells around the treatment zones show non-detect for diesel (Table 2-1).

Table 2-1. TPH-Diesel Sampling Results for Wells in Vicinity of Demonstration Area

Well Number	Location	TPH-Diesel Result (µg/L)	Sample Date
199-N-3	On plateau, upgradient of test areas	70 U[1]	3-10-09
199-N-96A	Along shoreline, immediately upriver of test areas	70 U[1]	6-18-09
199-N-123	Along shoreline, immediately downriver of test areas	75 U[1]	3-9-08[2]
N116mArray-1A	Aquifer tube downgradient of test areas	70 U[1]	6-17-09
N116mArray-2A	Aquifer tube downgradient of test areas	70 U[1]	6-17-09

[1] U = not detected above the minimum detection limit (MDL).

[2] Sampled last as part of CERCLA sampling in spring 2008, scheduled for CERCLA sampling again in FY2010.

The zones location upriver and outside the influence of the existing apatite PRB, while still within moderate strontium-90 plume concentration, and utilization of upriver aquifer tubes will provide analyses pertaining directly to this demonstration. These locations were also selected because of the large, flat areas that allow adequate clearance for vehicles or other equipment to pass by. The campaign to install an additional 171 injection and monitoring wells along the shoreline at 100-N was integrated with this demonstration in allowing core samples to be taken during drilling of selected wells located within the test areas and sent to PNNL for analysis. These analyses provide the technical verification of successful injection of phosphate and pre-formed apatite, and/or both, into the vadose zone.

The wider work area will allow the Contractor to have better control over any residual phosphate solution or pre-formed apatite that may upwell to the surface during injections. It is anticipated that a small amount of these solutions may penetrate the surface, although it is recommended that they be minimized (if not eliminated) and contained in a trench or shallow excavation allowing them to infiltrate into the vadose zone addressing the upper 1.5 ft bgs not initially treated by the injections. This trench or shallow excavation would then be backfilled to grade with the soil removed to construct it. Any waste generated during the jet injection demonstrations will be managed under DOE/RL-2000-41, *Interim Action Waste Management Plan for the 100-NR-2*

Operable Unit. Jet injection field work will be conducted under the current version of the CHPRC Soil and Groundwater Remediation Project's Health and Safety Plan and under the selected contractor's Job Safety Analysis.

Well locations will be provided to Ecology following completion of injections and each borehole will be decommissioned according to WAC 173-160 or to an Ecology-approved variance to WAC 173-160.

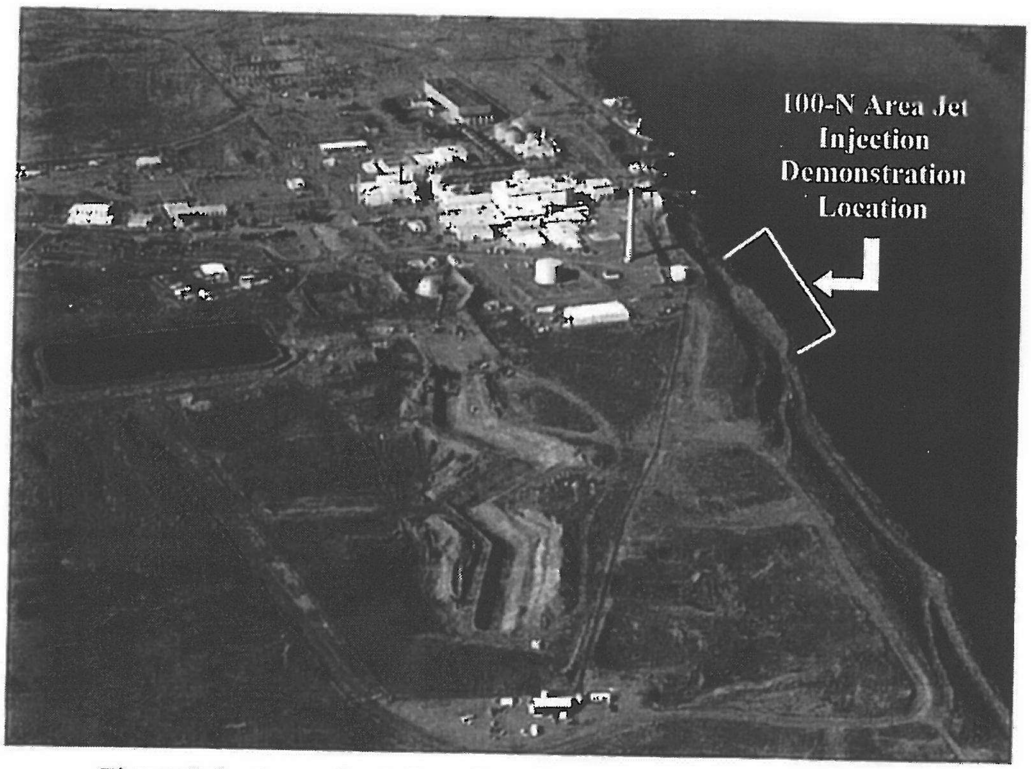

Figure 2-1. Approximate Locations for Jet Injection Demonstrations

2.2 PHOSPHATE TREATMENT ZONE

The first treatment zone will consist of a phosphate solution injected into the vadose zone (1.5 ft below ground surface [bgs] to the water table) and unconfined aquifer (water table to 25 ft bgs). The exact location(s), number of injections, and amount of solution will be stated in the Injection Plan.

2.2.1 Phosphate Solution

The solution that is to be injected within the phosphate treatment zone will consist of the following (resulting in a 100 mM aqueous solution under ambient test conditions):

- 85.3 mM disodium hydrogenphosphate (Na_2HPO_4)
    - FW 141.96 g/mol
    - Also called disodium phosphate, anhydrous
    - CAS registry **7558-79-4**

- 14.7 mM sodium dihydrogenphosphate (NaH_2PO_4)
  - FW 132.1 g/mol
  - Also called monosodium phosphate, anhydrous
  - CAS registry **7558-80-7**

The amount of phosphate solution to be injected within the treatment zone of 10 ft wide by 15 ft long from a depth of 1.5 ft bgs to 25 ft bgs, will be specified by Contractor to provide twice the required quantity to saturate the treatment zone based on an assumed 18% soil porosity and 130 pounds/cubic foot (lb/ft^3) soil density. Porosity values of 18% and 24% were determined for the Ringold Formation and Hanford formation, respectively, based on physical property measurements from sediment samples obtained during the drilling of characterization boreholes 199-N-122 and 199-N-123 in the 100-N Area of the Hanford Site (PNNL-17429). A soil density value of 129.5 lb/ft^3 is documented for sediments of the 116-K-2 Trench in the 100-K Area, immediately adjacent and upriver of the 100-N Area (WIDS). CHPRC, DOE, and Ecology will be able to evaluate and provide recommendations on phosphate amounts provided by Contractor.

2.2.2 Injection Strategy

The phosphate solution will utilize the existing calcium within the treatment zone to form reactive apatite and begin sequestering strontium-90. The development of in situ precipitation, for field injection and infiltration, has been optimized by utilizing the abundant calcium adsorbed to the arid Hanford sediments (and in groundwater). The stoichiometric ratio of calcium to phosphate used in solution (5:3) reflects the ratio of these chemicals in the apatite structure. Because considerable calcium is available from the sediment, experiments have shown that significantly less calcium-citrate was needed to form apatite in these studies. Recent investigations have also suggested that the proposed sodium phosphate solutions by themselves (at pH 7.5) will still form reactive apatite (PNNL-16891). The aforementioned phosphate solution and available calcium should result in a PRB containing approximately 4.0 mg apatite per g sediment in this treatment zone, which has the ability to incorporate all the strontium-90 that may pass the PRB for over 300 years.

Because this precipitation reaction will occur in situ, it is anticipated that some of the existing strontium-90 will immediately be incorporated into the apatite, resulting in a much faster sequestration rate. Data results from the initial low-concentration calcium-citrate-phosphate solution show that strontium-90 and other metals including aluminum, calcium, iron, manganese, and sodium increased due to the high ionic strength of the injection solution (PNNL-17429). The proposed phosphate solution, having a significantly lower ionic strength, is not expected to cause a substantial increase to strontium-90 or other groundwater metal concentrations as compared to the calcium-citrate-phosphate injections previously conducted at 100-NR-2. To evaluate this expectation, aquifer tube samples will be collected and analyzed for inductively coupled plasma plus mass spectrometry (ICP/MS) metals. The rate of adsorption of strontium-90 from phosphate solution injections is on the order of hours/days, while that for the calcium-citrate-phosphate solution was months/years. Another advantage of utilizing a jet grouting method of injection is that it can be conducted independent of river stage, although water table elevation should be considered during the development of the Injection Plan.

2.3 PHOSPHATE WITH ADDITION OF PRE-FORMED APATITE TREATMENT ZONE

The second treatment zone will consist of injection of the phosphate solution described in Section 2.1.1 into the vadose zone (1.5 ft bgs to the water table) and unconfined aquifer (water table to 25 ft bgs). Following injection of the phosphate solution, the pre-formed apatite described in Section 2.3.1 will be injected into the same treatment zone. The exact location(s), number of injections, and amount of phosphate and apatite will be stated in the Injection Plan.

2.3.1 Injection Strategy

The initial injection of phosphate will serve to address existing calcium as described in Section 2.1.2. The additional injection of apatite will provide the reactive surface area needed to adsorb strontium-90 and subsequently incorporate it into the apatite structure. The combination of these injections should produce a 4.0 mg apatite/g sediment PRB within this treatment zone, which has the ability to incorporate all the strontium-90 that may pass the PRB for over 300 years. The advantages of the jet injection of pre-formed apatite are that there is not a time delay in the formation of apatite, significant increases of strontium-90 are not expected due to the low ionic strength of the phosphate solution and pre-formed apatite, and it is independent of river stage.

2.4 APATITE TREATMENT ZONE

The third treatment zone will consist of a pre-formed apatite material injected into the vadose zone (1.5 ft bgs to the water table) and unconfined aquifer (water table to 25 ft bgs). The exact location(s), number of injections, and amount of solution will be stated in the Injection Plan.

2.4.1 Pre-formed apatite

The "solution" to be injected in the apatite and phosphate with addition of pre-formed apatite treatment zones will consist of a pre-formed apatite with the ability to sequester strontium-90 from the vadose zone and upper unconfined aquifer. The amount of pre-formed apatite to be injected in the target treatment zone (same size as described in Section 2.1), will be specified by Contractor to produce a 4.0 mg apatite per g sediment PRB in these treatment zones. The same assumptions on soil porosity and soil density apply.

2.4.2 Injection Strategy

Once injected, the pre-formed apatite will immediately begin incorporating the strontium-90 and should continue to do so for over 300 years assuming proper distribution within the vadose zone and upper unconfined aquifer.

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3.0 PERFORMANCE ASSESSMENT

The focus of this treatability test is to determine if jet injection technologies are capable of delivering phosphate and pre-formed apatite into the vadose zone and upper unconfined aquifer within the 100-N Area of the Hanford Site. The design criteria to achieve 4.0 mg apatite per g sediment will be the focal point in the performance evaluation of this test, but ultimately the reduction in strontium-90 concentration is most important.

3.1 SOIL SAMPLING AND ANALYSIS

During the installation of four of the 171 wells included in the *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan*, DOE/RL-2009-32, continuous core samples will be collected from the ground surface to total depth. The core locations will be selected to obtain information within the footprint of the three jet injection treatment zones (Figure 3-1). The field geologist will provide geologic logs of these core samples prior to their delivery to PNNL for analysis of, but not limited to, measurement of apatite per gram of sediment, hydraulic conductivity, strontium-90 concentration (gross beta), calcium concentration, and phosphate concentration. The determination of amount of apatite, the amount of strontium and strontium-90 incorporated, and treatment capacity will also be conducted by PNNL. If the field geologist suspects the presence of hydrocarbons during the drilling activities, based on field observations, samples will be collected and analyzed for TPH.

The PNNL selection of borehole sediment-core depths for strontium-90 and phosphate analysis will be at 2- to 3-foot intervals in the Hanford and Ringold formations, and in the fill. This provides a vertical profile in each borehole of strontium-90 (total and ion exchangeable) and phosphate using approximately ten random data points, which is sufficient for further analysis. Previous strontium-90 and phosphate measurements at this interval were used to calculate the subsurface mass of phosphate and strontium-90. For electron microprobe identification of the mineral phase apatite, only a few samples are needed to prove the injection results in the formation of apatite. A minimum of one random sample per borehole will be used as selected by PNNL.

These analyses will assess the effectiveness in the reduction of aqueous strontium-90 concentrations in the treatment area and the amount of apatite formed in the vadose zone following injections. Sampling and analysis requirements are contained in DOE/RL-2009-32, summarized below, and will also be included in the subsequent Field Test Instructions, completed following contract award.

A 10.2-cm (4-in.) inner-diameter core will be collected in 0.762-m (2.5-ft)-long runs; the split-spoon sampler will be lined with pre-cut 15.2-cm (6-in.)-long Lexan® liner sections. Upon retrieval of the sampler, the ends of each 15.2-cm (6-in.) core segment will be capped, and the liner will be labeled according to depth and well number. The core sections will also be labeled with an "up arrow" indicating core orientation. Once the core section has been appropriately labeled, end caps will be securely taped to prevent the caps from coming off during transport or storage. The soil core in the Lexan® liners will be analyzed as described above and in the following Table 3-1.

Table 3-1. Key Features of Sampling Design

Sampling Collection Methodology	Key Features of Design	Basis for Sampling Design	Sample Frequency	Depth Interval	Field QC	Analytes
Apatite Formation Testing						
Continuous core sampling	Collect continuous core samples during drilling of four wells (Figure 3-1)	Analyze soil core to determine apatite presence, presence of phosphate and calcium, strontium-90 concentrations, and strontium-90 adsorption into apatite	Continuous core samples from designated wells	From ground surface to total depth	--	Stronium-90 Apatite Calcium Strontium Phosphate

TBD = to be determined

QC = quality control

3.2 AQUIFER TUBE MONITORING

During the jet injection demonstrations, the aquifer tubes N116-1A and N116-2A (Figure 3-1) will be sampled and monitored for strontium-90, calcium, and phosphate as described in Tables 3-2 and 3-3. The sampling events will begin upon the first injection, occurring weekly for the first six weeks following completion of the three treatment zones, with a confirmatory sample being obtained in the third month. Previous work for the low concentration calcium-citrate-phosphate injections (PNNL-17429) have shown that if elevated strontium-90 and other metal concentrations are experienced, the aquifer stabilizes within a few weeks following injections. Gross beta analysis will initially be used for estimating strontium-90 concentrations to provide a quicker turn-around on analytical results. If the sampling personnel observe floating product during sampling activities, the samples will also be analyzed for TPH.

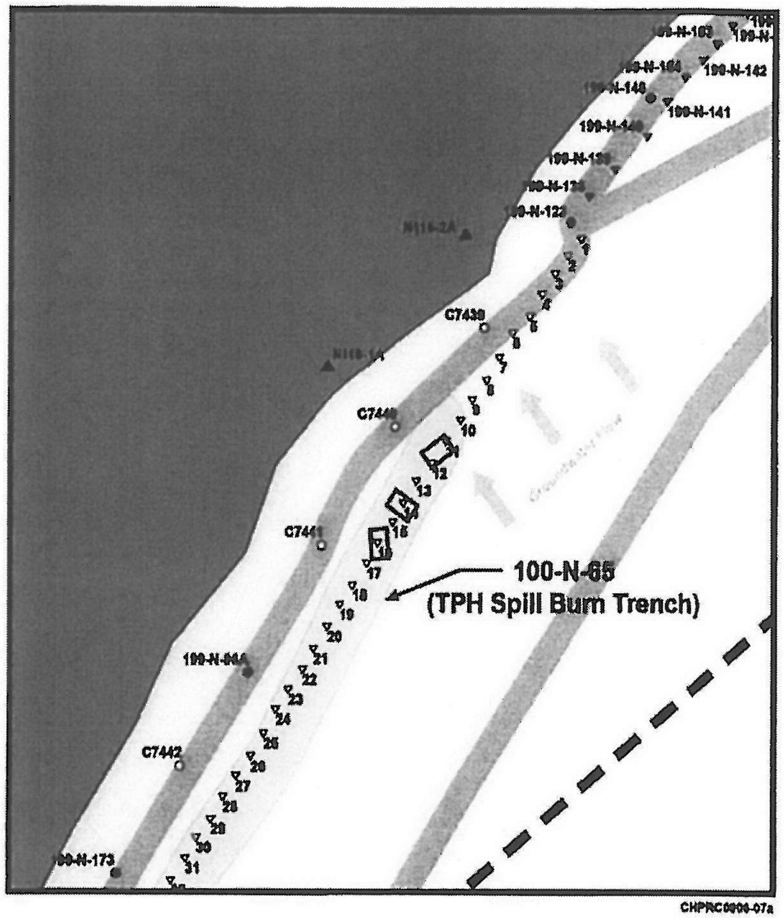

Figure 3-1. Site Plan – Proposed Locations of Jet Injection Demonstration Area in Relation to Existing Wells and Aquifer Tubes

Table 3-2. Jet Injection Test Sampling Requirements (Primary analytes shaded)

Parameter	Media / Matrix	Volume/Container	Preservation	Hold Time
Major Cations/metals: Al, As, B, Ba, Bi, Ca, Co, Cr, Fe, K, Mg, Mn, Ni, Zn, Zr, P, Sr, Na, Si, S, Sb	Water	20 mL plastic vial	Filtered (0.45 µm)[1], HNO_3 to pH <2	60 DAYS
Anions: Cl^-, Br^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^-	Water	20 mL plastic vial	Cool 4 °C	45 DAYS
Strontium-90 – PNNL Lab	Water	1 L plastic bottle	Filtered (0.45 µm)[1], HNO_3 to pH <2	60 DAYS
Gross Beta	Water	1 L plastic bottle	Filtered (0.45 µm)[1], HNO_3 to pH <2	60 DAYS
pH	Water	Field Measurement	n/a	n/a
Specific Conductance	Water	Field Measurement	n/a	n/a
Dissolved oxygen	Water	Field Measurement	n/a	n/a
Oxidation-Reduction Potential	Water	Field Measurement	n/a	n/a
Turbidity	Water	Field Measurement	n/a	n/a
Temperature	Water	Field Measurement	n/a	n/a

[1] Samples will be filtered (0.45 µm) following turbidity reading for increased sample quality

Table 3-3. Jet Injection Test Analytical Requirements (Primary analytes shaded)

Parameter	Analysis Method	Detection Limit or (Range)	Typical Precision / Accuracy	QC Requirements
Major cations/metals: Ca, Cr, Fe, K, Mg, P, Na, Si, S Al, B, Ba, Bi, Ni, Zn, Zr, Sr	ICP-OES, EPA Method 6010B or equivalent	1 mg/L 0.1 mg/L	± 10%	Daily Calibration; Blanks, Duplicates, and Matrix Spikes at 10% Level Per Batch of 20.
Anions: Cl^-. Br^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^-	Ion Chromatography, EPA Method 300.0A or equivalent	1 mg/L	± 15%	Daily Calibration; Blanks and Duplicates at 10% Level Per Batch of 20.
Strontium-90 – PNNL Lab	Separation followed by gross beta via liquid scintillation	75 pCi/L	± 15%	Daily Calibration; Blanks and Duplicates at 10% Level Per Batch of 20.
Gross Beta	Liquid scintillation	5 pCi/L	± 20%	Daily Calibration
pH	pH electrode	(2 to 12 units)	± 0.2 pH unit	User calibrate per manufacturer directions
Specific Conductance	Electrode	(0 to 100 mS/cm)	± 1% of reading	User calibrate per manufacturer directions
Dissolved oxygen	Membrane electrode	(0 to 20 mg/L)	± 0.2 mg/L	User calibrate per manufacturer directions
Oxidation-Reduction Potential	Electrode	(-999 to 999 mV)	± 20 mV	User calibrate per manufacturer directions
Turbidity	Turbidity meter	(0 to 1000 NTU)	± 3% of reading	User calibrate per manufacturer directions
Temperature	Thermocouple	(-5 to 50 °C)	± 0.2 °C	Factory calibration

3.3 ASSESSMENT/OVERSIGHT

Assessment and oversight activities evaluate the effectiveness of project implementation and associated QA and QC activities. The purpose of assessment is to ensure that the QAPjP is implemented as prescribed.

3.3.1 Assessments and Response Action

Contractor management, regulatory compliance, quality and /or health and safety organizations may conduct random surveillances and assessments to verify compliance with the requirements outline in this SAP, project work packages, the project quality management plan, procedures, and regulatory requirements.

Deficiencies identified by these assessments will be reported in accordance with existing programmatic requirements. The performing contractor's QA organization coordinates the corrective actions/deficiencies in accordance with the QA program. When appropriate, corrective actions will be taken by the Project Manager.

3.3.2 Reports to Management

Reports to management on data quality issues will be made if and when these issues are identified. These issues will be reported by laboratory personnel to the Sample Management and Reporting organization, who will then communicate the issues to the Project Manager. Subsequently, standard reporting protocols (e.g., project status reports) will be used to communicate these issues to management. Because performance or system assessments are not planned as part of this activity, the Project Manager will not be providing audit or assessment reports to management for this activity, unless an unanticipated request is made to conduct such an assessment. At the end of the project, a data quality assessment report will be prepared to evaluate whether the type, quality, and quantity of data that were collected meet the intent of the DQOs and SAP.

3.4 DATA MANAGEMENT

Analytical data resulting from the implementation of this QAPjP will be managed and stored in accordance with the applicable programmatic requirements governing data management procedures. At the direction of the Project Manager, all analytical data packages will be subject to final technical review by qualified personnel before they are submitted to the regulatory agencies or included in reports. Electronic data access, when appropriate, will be via a database (e.g., HEIS or a project specific database). Where electronic data are not available, hard copies will be provided in accordance with Section 9.6 of the Tri-Party Agreement.

Planning for sample collection and analysis will be in accordance with the programmatic requirements governing fixed laboratory sample collection activities, as discussed in the sample team's procedures. In the event that specific procedures do not exist for a particular work evolution, or it is determined that additional guidance to complete certain tasks is needed, written instructions will be developed to adequately control the activities, as appropriate. Examples of the sample team's requirements include activities associated with the following:

- Chain-of-custody/sample analysis requests
- Project and sample identification for sampling services
- Control of certificates of analysis
- Logbooks, checklists
- Sample packaging and shipping.

Approved procedures will be used to document field radiological measurements when this SAP is implemented. Examples of the types of documentation for field radiological data include the following:

- Instructions regarding the minimum requirements for documenting radiological controls information as per 10 CFR 835 ("Occupational Radiation Protection")

- Instructions for managing the identification, creation, review, approval, storage, transfer, and retrieval of primary contractor radiological records
- The minimum standards and practices necessary for preparing, performing, and retaining radiological-related records
- The indoctrination of personnel on the development and implementation of sample plans
- The requirements associated with preparing and transporting regulated material.

3.4.1 Resolution of Analytical System Errors

Errors reported by the laboratories are reported to the Sampling Coordinator, who initiates a Sample Disposition Record in accordance with the performing contractor's procedures. This process is used to document analytical errors and to establish resolution with the Project Manager.

3.5 DATA VALIDATION AND USABILITY

Data validation and usability activities occur after the data-collection phase of the project is completed. Implementation of these elements determines whether or not the data conform to the specified criteria, thus satisfying project objectives.

3.5.1 Data Review, Verification, and Validation

Data review, verification, and validation are performed on analytical data sets, primarily to confirm that sampling and chain-of-custody documentation is complete, sample numbers can be tied to the specific sampling location, samples were analyzed within required holding times, and analyses met the data quality requirements specified in the field sampling plan.

3.5.2 Verification and Validation Methods

Completed data packages will be validated by qualified Sample Management and Reporting personnel or by a qualified independent contractor. Validation will consist of verifying required deliverables, comparing requested versus reported analyses, and identifying transcription errors. Validation also will include evaluating and qualifying the results based on holding times, method blanks, laboratory control samples, laboratory duplicates, and chemical and tracer recoveries, as appropriate. No other validation or calculation checks will be performed. Level C data validation, as defined in the contractor's validation procedures (which are based on the EPA's functional guidelines [Bleyler 1988a, *Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses;* Bleyler 1988b, *Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses*]), will be performed for at least 5% of the data by matrix and analyte group. The goal is to cover the various analyte groups and matrices during the validation. When outliers or illogical results are identified in the data quality assessment, additional data validation will be performed. The additional validation will begin with Level C and may increase to Levels D and E as needed to ensure that the data are usable. Note that Level C validation is a review of the QC data, while Levels D and E include review of calibration data and calculations of representative samples from the data set. All data validation will be documented in data validation reports. With the exception of "R" qualified or rejected data, all data will be used. At least one data validation package will be generated. The validation requirements identified in this section are consistent with Level C validation, as defined in data validation procedures.

Relative to analytical data, physical data and/or field screening results are of lesser importance in making inferences of risk. Because of the secondary importance of such data, no validation for physical property data and/or field screening results will be performed; however, field QA/QC will be reviewed to ensure that the data are useable. Field instrumentation, calibration, and QA checks will be performed in accordance with the following:

- Calibration of radiological field instruments on the Hanford Site is performed under contract by PNNL, as specified in their program documentation.
- Daily calibration checks will be performed and documented for each instrument used to characterize areas that are under investigation. These checks will be made on standard materials that are sufficiently like the matrix under consideration so direct comparison of data can be made. Analysis times will be sufficient to establish detection efficiency and resolution.

The approval of field-data collection plans by the Radiological Lead represents the data validation and usability review for hand-held field radiological measurements.

3.6 DATA QUALITY ASSESSMENT

The data quality assessment process compares completed field sampling activities to those proposed in corresponding sampling documents and provides an evaluation of the resulting data. The purpose of the data evaluation is to determine if quantitative data are of the correct type and are of adequate quality and quantity to meet the project DQOs. *Data Quality Assessment: A Reviewer's Guide* (EPA/240/B-06/002) and *Data Quality Assessment: Statistical Methods for Practitioners* (EPA/240/B-06/003) will be used as guidance for the date quality assessment process.

4.0 REFERENCES

0078408, 2008. *Meeting Minutes, Unit Manager's Meeting, 100 & 300 Area Groundwater, Source Operable Units, Facility (D4 and ISS), and Mission Completion, May 8, 2008*, Washington Closure Hanford, Richland, Washington, May 8.

10 CFR 835, "Occupational Radiation Protection," *Code of Federal Regulations*.

Bleyler, R., 1998a. *Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses*, Hazardous Site Evaluation Division, U.S. Environmental Protection Agency, Washington D.C.

Bleyler, R., 1998b. *Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses*, Hazardous Site Evaluation Division, U.S. Environmental Protection Agency, Washington D.C.

DOE/RL-2000-41, *Interim Action Waste Management Plan for the 100-NR-2 Operable Unit*, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE/RL-2005-96, 2006. *Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit*, Rev. 0 REISSUE, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE/RL-2009-32, *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan*, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

EPA/ROD/R10-99/112, 1999. *Interim Remedial Action Record of Decision for the 100-NR-1 and 100-NR-2 Operable Units of the Hanford 100-N Area*, U.S. Environmental protection Agency, and Department of Energy, Olympia, Washington, as amended.

EPA/240/B-06/002, *Data Quality Assessment: A Reviewer's Guide*, EPA QA/G-9R, U.S. Environmental Protection Agency, Quality Assurance Division, Washington, D.C.

EPA/240/B-06/003, *Data Quality Assessment: Statistical Methods for Practitioners*, EPA QA/G-9S, U.S. Environmental Protection Agency, Quality Assurance Division, Washington, D.C.

Fluor/CH2M HILL, 2004. Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit. Letter Report. http://www.washingtonclosure.com/projects/endstate/risk_library.html#narea.

Lower, SK, PA Maurice, SJ Traina, and EH Carlson. 1998. "Aqueous Pb Sorption by Hydroxylapatite: Application of Atomic Force Microscopy for Containment and Stabilization of Contaminants." *Environmental Applications of Nanomaterials*, CRC Press, in press.

PNNL-16891, 2007, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO4 Solution Injection and Sr-90 Immobilization in 100-N Sediments*. Pacific Northwest National Laboratory, Richland, Washington.

PNNL-17429, 2008. *100-NR-2 Apatite Treatability Test: Low-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization.* Interim Report. Pacific Northwest National Laboratory, Richland, Washington.

PNNL-18303, 2009, *Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by surface Infiltration of a Ca-Citrate-Phosphate Solution*, Pacific Northwest National Laboratory, Richland, Washington.

Szecsody, J., J. Fruchter, C. Burns, M. Rockhold, M. Oostrom, M. Williams, V. Vermeul, and R. Moore, 2008, Sr-90 Immobilization by Infiltration of a Ca-Citrate-PO4 Solution into the Hanford 100N Area Vadose Zone. Waste Management 2008 Conference, Phoenix, AZ.

SOW, 2009. *Statement of Work: Apatite Barrier Construction Demonstration via Jet Injection.* CH2M HILL Plateau Remediation Company, Richland, Washington.

TAG, 2001. *Hanford 100-N Area Remediation Options Evaluation Summary Report.* Technical Advisory Group, November 2001.

Vukovic, Z., S Lazic, I Tutunovic, and S Raicevic. 1998. "On the Mechanism of Strontium Incorporation into Calcium Phosphates." *Journal of Serbian Chemical Society* 63.5: 387-393.

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